

CONDUCTIVE ADHESIVE

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Inventor: ABE SHINICHI; others: 02
Applicant: HOKURIKU TORYO KK
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Abstract of JP7216330

PURPOSE: To obtain a conductive adhesive which can bond an electrode to a charge collector inseparably and scarcely causes the separation of the carbon particles when applied by mixing a specified organic resin with carbon particles.

CONSTITUTION: This adhesive comprises 50-85wt.% copolymer prepared by copolymerizing 70-99.99mol% aliphatic hydrocarbon monomer having an ethylenic unsaturation or conjugated double bonds with 0.01-20mol% ethylenically unsaturated monomer having one or two carboxyl groups or one or two acid anhydride groups to be hydrolyzed later or having a hydroxyl group bonded to the carbon atom at which no aliphatic carbon-carbon unsaturated bond is present or a salt of this copolymer and carbon particles having a particle size of 0.1µm or below and a pH of 6-9 when measured in the form of a dispersion prepared by dispersing 10wt.% particles in an ethanol/water mixture (1:1 by weight).

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(71)出願人 591252862
北陸塗料株式会社
新潟県新潟市濁川3993番地
(72)発明者 阿部 真一
新潟県新潟市濁川3993番地 北陸塗料株式
会社内
(72)発明者 横山 公憲
新潟県新潟市濁川3993番地 北陸塗料株式
会社内
(72)発明者 鈴木 憲一
新潟県新潟市濁川3993番地 北陸塗料株式
会社内
(74)代理人 弁理士 津国 肇 (外2名)

(54)【発明の名称】 導電性接着剤

(57)【要約】

【構成】 有機樹脂と炭素粒子を含有する導電性組成物であって、有機樹脂が脂肪族炭化水素モノマー単位とカルボキシル基もしくは側鎖炭素原子に結合する水酸基を有するモノマー単位とを含む共重合体またはその塩であり、炭素粒子の大きさが0.1 μ m 以下で、エタノール：水混液のpHを6～9とし、有機樹脂の量が50～85重量%である導電性接着剤。

【効果】 炭素粒子が分離しにくく、優れた接着力を有し、電極と集電体との剥離を生ずることなく、高容量を保持できる。

脂は、必要に応じて他のモノマーに由来する単位を含んでもよく、また、直接に(1)と(2)の共重合によって得られるほか、加水分解、水素添加および／またはアンモニウム塩やアミン塩の形成反応を経て合成してもよい。このような構成の共重合体を用いることにより、モノマー(1)に由来する単位によって、充放電サイクルやヒートサイクルに起因する電極の膨張、収縮の応力を吸収することができ、モノマー(2)に由来する単位によって、集電体の金属に対する優れた接着性を有する導電性接着剤が得られる。

【0010】(1)の脂肪族炭化水素モノマーとしては、エチレン性不飽和二重結合または共役二重結合を有する脂肪族炭化水素が用いられる。具体的には、エチレン、プロピレン、ブテン-1、イソブテン、ペンテン-1、1-メチルペンテン-1、ブタジエンおよびイソブレンが挙げられ、ブタジエンまたはイソブレンを用いた場合、共重合後に水素添加によって飽和化してもよい。これらは単独で用いても、2種以上を併用しても差支えなく、エチレン、プロピレンおよびブタジエン(共重合後、飽和化する)が好ましい。

【0011】このモノマー(1)は、共重合にあずかるモノマーの70~99.99モル%であり、好ましくは75~99.9モル%、さらに好ましくは77~99.5モル%である。(1)が70モル%未満では、共重合体が電極の体積膨張、収縮による応力を吸収する能力に欠け、電極の充放電サイクルやヒートサイクルによって、使用中に剥離を生ずる。99.99モル%を越えると、集電体のような金属に対する接着性が劣る。

【0012】(2)のモノマーとしては、カルボキシル基含有モノマーとして、アクリル酸、メタクリル酸、クロトン酸、マレイン酸、イタコン酸、4-カルボキシステレンなどが例示される。後に加水分解によって2個のカルボキシル基を生ずる酸無水物基を有するモノマーとして、無水マレイン酸、イタコン酸無水物、 Δ^4 テトラヒドロフタル酸無水物など；およびシクロペンタジエンとイタコン酸無水物とのディールス・アルダー反応付加物などが例示される。また、水酸基含有モノマーとして、2-ヒドロキシエチルアクリレート、2-ヒドロキシエチルメタクリレート、3-ヒドロキシプロピルアクリレート、3-ヒドロキシプロピルメタクリレート、4-ヒドロキシステレンなどの、脂肪族性炭素-炭素不飽和結合の存在しない炭素原子、すなわち、重合体を形成した後に側鎖に位置する炭素原子に水酸基が結合したモノマーが例示される。これらは単独で用いても、2種以上を併用しても差支えなく、アクリル酸、無水マレイン酸および4-ヒドロキシステレンが好ましい。(2)として酸無水物基を有するモノマーを用いたときは、次に加水分解の工程を加えることによって、2個のカルボキシル基に転換する。

【0013】このモノマー(2)は、共重合にあずかる

モノマーの0.01~20モル%である。カルボキシル基含有モノマーおよび酸無水物含有モノマーの場合、0.05~10モル%が好ましく、0.1~5モル%がさらに好ましい。水酸基含有モノマーの場合、0.1~15モル%が好ましく、1~10モル%がさらに好ましい。0.01モル%未満では集電体のような金属に対する接着性が劣り、20モル%を越えると、電極の体積膨張、収縮による応力を吸収しきれなくなる。

【0014】さらに、共重合体には、必要に応じて、エチレン性不飽和二重結合を有する他のモノマー単位を、30モル%以下含むことができる。このような単位を導入するためのモノマーとしては、スチレン、アクリロニトリルおよび側鎖に水酸基を含まない(メタ)アクリル酸エステル、例えばメチルアクリレート、メチルメタクリレート、エチルアクリレート、エチルメタクリレート、ブチルアクリレート、ブチルメタクリレートなどが例示される。これらが30モル%を越えると、共重合体が電解液に膨潤または溶解して、バインダーとしての機能を果たさなくなる。別のモノマーのもうひとつの例としてフッ化ビニリデンが挙げられる。これが30モル%を越えると、共重合体の接着力が低下し、また導電ペーストを調製する際に、芳香族炭化水素に溶解しにくくなる。

【0015】このような要件(A)を満たす共重合体である有機樹脂は、(1)のモノマー、(2)のモノマー、および必要に応じてその他のモノマーから、常法によって共重合させて得ることができる。さらに、(1)のモノマーの一部もしくは全部としてブタジエンまたはイソブレンのような共役ジエンを用いたときは、ポリマー鎖に残存する二重結合に無水マレイン酸のような酸無水物基を有する(2)のモノマーを付加した後、加水分解して、マレイン酸単位に転換する。また、同様に共役ジエンを用いて得られたポリマー鎖の二重結合を、水素添加によって飽和化してもよい。さらに、得られた共重合体がカルボキシル基含有単位を含む場合に、これをアルカリ金属アンモニウム塩や有機アミンによって、アンモニウム塩やアミン塩にしてもよい。

【0016】本発明の導電性接着剤に導電粒子として用いられる炭素粒子は、エタノール-水の重量比1:1の混合液に10重量%分散させたときに、該混合液のpHを6~9、好ましくは6.5~8.8にする、中性ないし弱アルカリ性のものである。pHが6未満では炭素粒子が沈降、分離しやすく、とくに見掛け粘度20Pa・s以下の導電ペーストを調製した場合、放置中に炭素粒子の凝集、炭素粒子と有機樹脂、溶媒との分離を起こす。一方、pHが9を越えても、炭素粒子の凝集、沈降が起こる。炭素粒子の形状は、球状、りん片状、繊維状のいずれでもよい。その大きさ、すなわち球状のものは直径と短径の平均、りん片状のものは扁平面の長径と短径の平均、繊維状のものは長さが0.1 μ m以下、好ましくは

30～90nm、より好ましくは35～80nmである。そのことによって、バインダーである有機樹脂への分散性を上げ、沈降を防止することができる。

【0017】本発明の導電性接着剤は、それぞれ上述の条件を満たす有機樹脂と炭素粒子を含む。有機樹脂の配合量は、該接着剤中、50～85重量%、好ましくは55～75重量%である。50重量%未満では炭素粒子の吸油量が多く、塗布むらを起こす。85重量%を越えると体積抵抗率が高くなり、容量の減少をもたらす。

【0018】本発明の導電性接着剤の有機樹脂を溶解させ、炭素粒子を分散させるために、溶媒を加えて、処理に適する見掛け粘度を有する導電ペーストを調製することができる。溶媒としては、トルエン、キシレン、エチルベンゼン、石油留分の芳香族成分のような芳香族炭化水素類；およびヘキサン、ヘプタン、オクタン、シクロヘキサン、ミネラルスピリット、灯油のような脂肪族炭化水素類が例示される。有機樹脂中にカルボキシル基や水酸基が多い場合は、有機樹脂の溶解を助けるために、5～20重量%のプロパノールまたはブタノールを併用してもよい。

【0019】導電ペーストの見掛け粘度は、塗布により薄膜を形成するように、10Pa・s以下が好ましい。

【0020】本発明の導電性接着剤には、その目的に反しないかぎり、必要に応じて、ニトリルゴム、イソプレンゴム、エチレンプロピレンゴムなどを配合してもよい。

【0021】本発明の導電性接着剤および導電ペーストは、有機樹脂、炭素粒子および必要に応じてその他の成分を、プロペラ攪拌器、デソルバー、ニーダー、らい解機、三本ロール、ボールミルのような混合分散機によって混合、分散させることによって調製できる。

【0022】塗布は、ディスペンサまたはアプリケーションによる塗布；スクリーン印刷または孔版印刷による印刷など、薄膜状に塗布が可能な任意の方法を用いてよい。接着層の厚さは10μm以下が好ましい。10μmを越えると、抵抗による損失が大きい。

【0023】本発明の導電性接着剤を用いた導電ペーストを電極と集電体の接着に使用して、各種のエネルギー貯蔵素子を作製することができる。該エネルギー貯蔵素子のその他の要素は、公知のものを使用して差支えない。

【0024】

【発明の効果】本発明によって、保存中および塗布の際に炭素粒子の分離が起こりにくい、優れた接着性と安定した導電性を有する導電性接着剤が得られる。本発明の導電性接着剤によって電極と集電体を接着した各種の電池や電気二重層コンデンサなどのエネルギー貯蔵素子は、充放電サイクルやヒートサイクルによる電極の膨張、収縮の応力を吸収し、電極と集電体との間の剥離を生ずることなく、高容量を維持できる。したがって、本

発明の導電性接着剤は、リチウム電池、ニッケル水素電池をはじめとする各種の電池ならびにコンデンサなど、広くエネルギー貯蔵素子に応用できる。

【0025】

【実施例】以下、本発明を実施例および比較例によって詳細に説明する。これらの例で、部は重量部を表す。本発明はこれらの実施例によって限定されるものではない。

【0026】以下の例で、炭素粒子のpHは、下記のようにして測定した。すなわち、エタノールと水の重量比1：1の混合液に、その10重量%の炭素粒子を分散させ、5分間放置した。ついで、遠心分離によって炭素粒子を除去し、該混合液のpHをpHメーターで測定した。

【0027】参考例：有機樹脂の合成

表1に示すモノマー組成の共重合体B1～B3を、「高分子合成の実験法」（大津隆行、木下雅悦著、化学同人発行）に記載された方法に準じて、オートクレーブを用い、高圧下、アゾビスイソブチロニトリルの存在下に、ベンゼン中でラジカル重合を行った。合成したモノマーを、無水ジエチルエーテル中に投入してポリマーを沈殿させることによって精製し、乾燥した。

【0028】

【表1】

表1

バ イ ン ダ ー No.		B 1	B 2	B 3	B 4
モノ マ ー (部)	エチレン プロピレン ブテン-1 ブタジエン	49.5 50		47 50	47.5 47.5
	4-ヒドロキシスチレン アクリル酸 無水マレイン酸	0.5	1.5	3	5
	スチレン		20		

【0029】実施例1～5、比較例1、2：電気二重層コンデンサ

比表面積2,000m²/gの活性炭を、錠剤成形機で、直径10mm、厚さ1mmに成形して、電極とした。表2に示す組成により、参考例で合成したカルボキシル基を有する有機樹脂B1～B4を、それぞれ130～180℃の沸点範囲を示す芳香族石油留分に溶解させた。また比較のための有機樹脂であるレゾール型フェノール樹脂B5をエチレングリコールジエチルエーテルに溶解させた。これに表2に示す炭素粒子をそれぞれ添加して、三本ロールによって炭素粒子が系に均一に分散するまで混合することにより、導電ペーストを調製した。この導電ペーストを常温で24時間放置して、炭素粒子の分離の度合いを観察した。その結果は、表2に示すとおりであっ

た。

【0030】この導電ペーストを、ステンレス製の集電体に、乾燥後の塗膜厚さが $2 \sim 4 \mu\text{m}$ になるようにスクリーン印刷し、ついで上記の電極を圧着し、 130°C で15分の加熱乾燥を行って、電極と集電体とを接着した。ただし、実施例4は 120°C で30分の加熱乾燥を行った後、 150°C の熱板上で接着を行った。また比較例2は、 200°C で30分加熱することによって硬化させた。このようにして得られた接着層について、体積抵抗率を測定した。

【0031】このように接着された炭素電極と集電体を、ポリプロピレン多孔質フィルムからなるセパレータを介して、電極を向かい合わせにして圧着して、プロピレンカーボネートとジメトキシエタンのモル比1:1の

混合液1, 000mlに過塩酸テトラエチルアンモニウムを1モル溶解させて調製した電解液で充たし、電気二重層コンデンサとした。このようにして得られたコンデンサの容量について、特開平2-2186808号公報に記載されている方法により、初期値、および温度 -20°C で30分、温度 90°C で30分を1サイクルとして50サイクルのヒートサイクル後の値を測定した。また、上記のヒートサイクル試験後の電極の状態を観察した。

【0032】これらの結果を、本発明の導電製接着剤を用いた実施例1~4と、pHの低い炭素粒子を用いた比較例1、および有機樹脂としてレゾール型フェノール樹脂を用いた比較例2と比較して、表2に示す。

【0033】

【表2】

表2

			実 施 例					比較例	
			1	2	3	4	5	1	2
組 成	有機樹脂	種 類 (部)	B1 60	B1 70	B3 70	B2 70	B4 55	B1 70	B5 70
	炭素粒子	大きさ (Å)	400	400	400	760	760	180	400
		pH	6.8	6.8	6.8	7.5	7.5	3.2	6.8
		量 (部)	40	30	30	30	45	30	30
不揮発分 (重量%)			41	39	42	42	34	37	43
導電ペーストの安定性 ^{*1}			○	○	○	○	○	×	○
塗膜厚さ (μm)			3	4	4	4	4	4	3
体積抵抗率 ($\Omega \cdot \text{cm}$)			1.0	1.5	1.7	1.2	1.3	0.7	0.2
容量 (F) , 初期値			1.5	1.4	1.5	1.5	1.3	1.5	1.5
ヒートサイクル後			1.5	1.4	1.5	1.5	1.3	1.4	0.3
電極の状態 ^{*2}			○	○	○	○	○	○	×

(注) *1 ○:分離せず; ×:分離

*2 ヒートサイクル後、○:以上なし; ×:剥離発生

JP-A No. 7-216330

(54) [TITLE OF THE INVENTION] CONDUCTIVE ADHESIVE

(57) [ABSTRACT]

[CONSTITUTION] A conductive adhesive which is a conductive composition comprising an organic resin and carbon particles, wherein the organic resin is a copolymer having an aliphatic hydrocarbon monomer unit and a monomer unit having a carboxyl group or a hydroxyl group bonded to a side chain hydrocarbon atom or its salt, the carbon particle has a size of 0.1 μm or less, the pH of an ethanol-water mixture solution is made to be 6 or 9 and the amount of the organic resin is 50 to 85% by weight.

[EFFECT] The conductive adhesive is resistant to the separation of carbon particles, has excellent adhesion, is resistant to the peeling of an electrode from a current collector and can retain high capacity.

[SCOPE OF CLAIM FOR PATENT]

[Claim 1]

A conductive adhesive which is a conductive composition comprising an organic resin and carbon particles, wherein the organic resin fulfills the following requirement (A), the carbon particles fulfill the following requirement (B) and the amount of the organic resin is 50 to 85% by weight:

(A) the organic resin is a copolymer obtained by copolymerizing (1) 70 to 99.99 mol% of one or two or more aliphatic hydrocarbon monomers having an ethylenic unsaturated double bond or a conjugate double bond with (2) 0.01 to 20 mol% of one or two or more ethylenic unsaturated double bond-containing monomers which have one or two or more carboxyl groups or an acid anhydride group which is to be hydrolyzed afterwards in its

molecule or a hydroxyl group bonded with a carbon atom free from the presence of an aliphatic carbon-carbon unsaturated bond, or its salt; and

(B) (i) the pH of a solution obtained by dispersing 10% by weight of the carbon particles in a mixture solution of ethanol and water (1 : 1, (ratio by weight)) is 6 to 9, and (ii) the carbon particle has a size of 0.1 μm or less.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[INDUSTRIAL APPLICABLE FIELD]

The present invention relates to a conductive adhesive suitable as an adhesive used to stick an electrode to a current collector in energy storing elements such as lithium batteries, nickel-hydrogen batteries and electric double-layer capacitors.

[0002]

[CONVENTIONAL ART]

It is well known to use a carbon material for the negative electrode of a lithium battery (see JP-A 63-24555 and JP-A 64-7258). Batteries of this type are listed in Report of Government Industrial Research Institute, Osaka, vol. 42, pp150-159 (1992). As to the lithium batteries, for example, a separator made of a porous polyolefin is interposed between a positive electrode and a negative electrode and both electrodes are wound spirally to fabricate a battery. At this time, an adhesive material containing carbon particles and a polyvinylidene fluoride is used as the conductive adhesive for sticking the electrode to the current collector.

[0003]

This polyvinylidene fluoride has low adhesion to a metal. Therefore, when

charging and discharging are repeated, the outermost periphery of the electrode is peeled from the current collector, bringing about reduced battery capacity.

[0004]

In coin type electrodes and electric double-layer capacitors, conductive adhesives using resins and carbon materials are also used to stick an electrode punched pellet-wise to a current collector. As the resin, a phenol resin is used because of low volume resistance. However, while a heat cycle and a charge and discharge cycle are repeated, the electrode is peeled from the current collector or broken, causing a reduction in capacity.

[0005]

When a conductive adhesive containing carbon particles is applied to a metal material such as an aluminum clad material and a stainless cell, usually, a conductive paste having a viscosity of 0.01 to 20 Pa·s is prepared using a solvent and applied. Because a polytetrafluoroethylene is insoluble in a solvent, a polytetrafluoroethylene powder having a diameter of several μm is dispersed together with carbon particles in a solvent prior to application. Such a dispersion solution tends to produce precipitates of the carbon particles or polytetrafluoroethylene powder and it is therefore difficult to preserve and handle the dispersion solution. The polyvinylidene fluoride is dissolved in polar solvents such as 2-methylpyrrolidone but precipitates when the solvent absorbs moisture. Furthermore, carbon particles having a particle diameter of 0.1 μm or more tend to precipitate in a solvent, whereas carbon particles having a particle diameter less than 0.1 μm have the problem that if these particles are passed through a three-roll

when a conductive paste is prepared, they absorb moisture, leading to precipitation of a resin.

[0006]

[PROBLEM TO BE SOLVED BY THE INVENTION]

It is an object of the present invention to provide a conductive adhesive which is used to stick an electrode to a current collector in an energy storing element such as a battery or a capacitor, the adhesive preventing the electrode from being peeled from the current collector and being resistant to separation of carbon particles when being applied between the electrode and the current collector.

[0007]

[MEANS FOR SOLVING THE PROBLEM]

The present inventors have made earnest studies to solve the above problem and, as a result, found that the above object can be attained by using, as the organic resin binder, a copolymer obtained by combining a unit capable of absorbing stress generated by the expansion and shrinkage of an electrode caused by a charge discharge cycle and a heat cycle with a unit having a group providing the adhesion of the current collector to a metal in its molecule and by using carbon particles having a predetermined pH range and a predetermined particle size as the conductive particles, to complete the present invention.

[0008]

Accordingly, the present invention relates to a conductive adhesive which is a conductive composition comprising an organic resin and carbon particles, wherein the organic resin fulfills the following requirement (A), the carbon

particles fulfill the following requirement (B) and the amount of the organic resin is 50 to 85% by weight:

(A) the organic resin is a copolymer obtained by copolymerizing (1) 70 to 99.99 mol% of one or two or more aliphatic hydrocarbon monomers having an ethylenic unsaturated double bond or a conjugate double bond with (2) 0.01 to 20 mol% of one or two or more ethylenic unsaturated double bond-containing monomers which have one or two or more carboxyl groups or an acid anhydride group which is to be hydrolyzed afterwards in its molecule or a hydroxyl group bonded with a carbon atom free from the presence of an aliphatic carbon-carbon unsaturated bond, or its salt; and

(B) (i) the pH of a solution obtained by dispersing 10% by weight of the carbon particles in a mixture solution of ethanol and water (1 : 1, (ratio by weight)) is 6 to 9, and (ii) the carbon particle has a size of 0.1 μm or less.

[0009]

The organic resin used as the binder in the conductive adhesive of the present invention is a copolymer of the above aliphatic hydrocarbon monomer (1) and the above monomer (2) having a carboxyl group, acid anhydride group or hydroxyl group. The organic resin may contain a unit derived from other monomers according to the need. Besides the case where the organic resin is obtained by direct copolymerization of the above (1) and (2), the organic resin may be synthesized through hydrolysis, hydrogenation and/or an ammonium salt or amine salt formation reaction. When the copolymer having such a structure is used, a conductive adhesive is obtained which can absorb the expansion and shrinkage stress caused by a charge and discharge cycle or a heat cycle due to the unit derived from the

monomer (1) and which has high adhesion of the current collector to a metal due to the unit derived from the monomer (2).

[0010]

As the aliphatic hydrocarbon monomer (1), an aliphatic hydrocarbon having an ethylenic unsaturated double bond or a conjugate double bond is used. Examples of the aliphatic hydrocarbon monomer include ethylene, propylene, butene-1, isobutene, pentene-1, 1-methylpentene-1, butadiene and isoprene. When butadiene or isoprene is used to form a copolymer, the copolymer may be saturated by hydrogenation after the copolymer is formed. These aliphatic hydrocarbons may be used either independently or in combinations of two or more. Among these hydrocarbons, ethylene, propylene and butadiene (saturated after copolymerized) are preferable.

[0011]

The amount of this monomer (1) is 70 to 99.99 mol%, preferably 75 to 99.9 mol% and more preferably 77 to 99.5 mol% of the monomers subjected to copolymerization. When the amount of (1) is less than 70 mol%, the copolymer is lacking in the ability of absorbing the stress produced by the volume expansion and shrinkage of the electrode, giving rise to the peeling of the electrode caused by charge and discharge cycle or heat cycle during the operation of the electrode. When the amount exceeds 99.99 mol%, adhesion to a metal such as the current collector is inferior.

[0012]

Examples of the monomer (2) include acrylic acids, methacrylic acids, crotonic acid, maleic acid, itaconic acid and 4-carboxystyrene as the carboxyl group-containing monomer, maleic acid anhydride, itaconic acid anhydride

and Δ^4 tetrahydrophthalic acid anhydride; and Diels-Alder reaction adducts of cyclopentadiene and itaconic acid anhydride as the monomer having an acid anhydride group producing two carboxyl groups afterwards by hydrolysis. Examples of the monomer (2) also include, as the hydroxyl group-containing monomer, monomers in which a hydroxy group is bonded with a carbon atom free from the presence of an aliphatic carbon-carbon atom, specifically, a carbon atom positioned at the side chain after the polymer is formed: examples of these monomers include 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 3-hydroxypropylacrylate, 3-hydroxypropylmethacrylate and 4-hydroxystyrene. These compounds may be used either singly or in combinations of two or more. Acrylic acids, maleic acid anhydride and 4-hydroxystyrene are preferable. A monomer having an acid anhydride group is used as (2), the acid anhydride group is converted into two carboxyl groups by adding a hydrolysis process next.

[0013]

The amount of the monomer (2) is 0.01 to 20 mol% of the monomers subjected to copolymerization. In the case of the carboxyl group-containing monomer or acid anhydride-containing monomer, the amount of each monomer is preferably 0.05 to 10 mol% and more preferably 0.1 to 5 mol%. In the case of the hydroxyl group-containing monomer, the amount of the monomer is preferably 0.1 to 15 mol% and more preferably 1 to 10 mol%. When the amount is less than 0.01 mol%, adhesiveness to a metal such as the current collector is inferior whereas when the amount exceeds 20 mol%, the resulting copolymer will fail in absorbing the stress caused by the

volume expansion and shrinkage of the electrode.

[0014]

Moreover, the copolymer may contain 30 mol% or more of other monomer units having an ethylenic unsaturated double bond. Examples of the monomer for introducing such a unit include styrene, acrylonitrile and (meth)acrylates containing no hydroxyl group at the side chain such as methylacrylate, methylmethacrylate, ethylacrylate, ethylmethacrylate, butylacrylate and butylmethacrylate. If the amount of these monomers exceeds 30 mol%, the copolymer is swelled or dissolved in the electrolytic solution so that it does not function as a binder resultantly. As another example of the monomer, vinylidene fluorides are given. When the amount of this monomer exceeds 30 mol%, the adhesion of the copolymer is reduced and also, the copolymer is scarcely dissolved in an aromatic hydrocarbon when a conductive paste is prepared.

[0015]

The organic resin that is the copolymer fulfilling the requirement (A) may be obtained from the monomer (1) and the monomer (2) and, as required, other monomers by copolymerizing these monomers according to a usual method. When a conjugate diene such as butadiene or isoprene is used as a part or all of the monomer (1), the monomer (2) having an acid anhydride group such as maleic acid anhydride is added to a double bond left on a polymer chain and then hydrolyzed to convert it into a maleic acid unit. Also, a double bond of a polymer chain obtained likewise using a conjugate diene may be saturated by hydrogenation. Moreover, when the resulting copolymer contains a carboxyl group-containing unit, this may be made into

an ammonium salt or an amine salt by using an alkali metal ammonium salt or an organic amine.

[0016]

The carbon particles used as the conductive particles in the conductive adhesive of the present invention is a neutral or weakly alkaline one which allows a mixture solution to have a pH range from 6 to 9 and preferably 6.5 to 8.8, the mixture solution being obtained by dispersing these particles in an amount of 10% by weight in a mixture of ethanol and water (1 : 1, weight ratio). When the pH is less than 6, the carbon particles are easily precipitated and separated. When, particularly, a conductive paste having an apparent density of 20 Pa·s or less, the carbon particles are coagulated and the carbon particles are separated from the organic resin or the solvent while the solution is allowed to stand. When the pH exceeds 9, on the other hand, coagulation and precipitation of the carbon particles are also caused. The carbon particles may have any of a sphere form, flake form and fibrous form. The size of the carbon particle is preferably 0.1 μm or less, preferably 30 to 90 nm and more preferably 35 to 80 nm as an average of the diameter and minor axis in the case of a spherical one, as an average of the diameter and minor axis of a flat surface in the case of a flake one and as the length in the case of a fibrous one. This limitation makes it possible to improve the dispersibility of the particles in the organic resin that is the binder and to prevent precipitation of the particles.

[0017]

The conductive adhesive of the present invention contains the organic resin and carbon particles which respectively satisfy the aforementioned

requirements. The amount of the organic resin to be compounded is 50 to 85% by weight and preferably 55 to 75% by weight in the adhesive. When the amount is less than 50% by weight, the oil absorption of the carbon particles is large, causing coating unevenness. When the amount exceeds 85% by weight, the volume resistance is increased, bringing about a reduction in capacity.

[0018]

A solvent may be added to dissolve the organic resin of the conductive adhesive of the present invention to disperse the carbon particle, thereby preparing a conductive paste having an apparent density suitable to treatment. Examples of the solvent include aromatic hydrocarbons such as toluene, xylene, ethylbenzene and aromatic components of petroleum fractions; and aliphatic hydrocarbons such as hexane, heptane, octane, cyclohexane, mineral spirit and kerosene. When many carboxyl groups and hydroxyl groups are present in the organic resin, 5 to 20% by weight of propanol or butanol may be used together to stimulate the dissolution of the organic resin.

[0019]

The apparent viscosity of the conductive paste is preferably 10 Pa·s or less to form a thin film.

[0020]

Nitrile rubber, isoprene rubber, ethylene propylene rubber or the like may be compounded insofar as it is not contrary to the object of the present invention.

[0021]

The conductive adhesive and conductive paste according to the present invention may be prepared by mixing and dispersing the organic resin, the carbon particles and, according to the need, other components by a mixing/dispersing machine such as a propeller stirrer, desorber, kneader, dissolver, three-roll or ball mill.

[0022]

As to the coating method, any optional method enabling the application of a thin film may be used: these methods including application using a dispenser or an applicator; and printing such as screen printing or perforated plate printing. The thickness of the adhesive layer is preferably 10 μm or less. When the thickness exceeds 10 μm , this results in a large resistance loss.

[0023]

Various energy storing elements can be manufactured by using a conductive paste utilizing the conductive adhesive of the present invention for bonding an electrode with a current collector. As other elements of these energy storing elements, known ones may be used without any problem.

[0024]

[EFFECT OF THE INVENTION]

The present invention ensures that a conductive adhesive which is resistant to separation of carbon particles when stored and applied and has excellent adhesiveness and stable conductivity is obtained. Energy storing elements such as various batteries and electric double-layer capacitors in which the electrode is bound with the current collector by the conductive adhesive of the present invention absorb the stress of expansion and shrinkage of the

electrode caused by charge and discharge cycles and heat cycles and therefore prevent the electrode from being peeled from the current collector, with the result that high capacity can be maintained. As a consequence, the conductive adhesive of the present invention can be widely applied to energy storing elements, for example, various batteries including lithium batteries and nickel hydrogen batteries and capacitors.

[0025]

[EXAMPLES]

The present invention will be hereinafter described in detail by way of examples and comparative examples. In these examples, all designations of "parts" indicate parts by weight. These examples are not intended to be limiting of the present invention.

[0026]

In the following examples, the pH of the carbon particles was measured in the following manner. Specifically, to a mixture solution of ethanol and water (ratio by weight: 1 : 1) were added and dispersed carbon particles in an amount of 10% by weight based on the mixture solution and the mixture was allowed to stand for 5 minutes. Then, carbon particles were removed by centrifugation to measure the pH of the mixed solution by a pH meter.

[0027]

Reference Example: Synthesis of organic resin

Copolymers B1 to B3 having each monomer composition shown in Table 1 were radically polymerized using an autoclave under high pressure in the presence of azobisisobutyronitrile in benzene according to the method described in "Polymer Synthesis, Experimental Method" (OTSU Takayuki &

KINOSHITA Masaetsu, Published by Kagaku Dojin). The synthesized monomer was poured in anhydrous diethyl ether to precipitate a polymer, thereby refining the reaction product. The polymer was dried.

[0028]

Table 1

	Binder No.	B1	B2	B3	B4
Monomer (parts)	Ethylene	49.5		47	47.5
	Propylene	50			47.5
	Butene-1			50	
	Butadiene		78.5		
	4-hydroxystyrene				5
	Acrylic acid	0.5	1.5		
	Maleic acid anhydride			3	
	Styrene		20		

[0029]

Examples 1 to 5, Comparative Examples 1 and 2: Electric double-layer capacitor

Activated carbon having a specific surface area of 2,000 m²/g was molded into the following size: diameter: 10 mm and thickness: 1 mm by a tablet machine to form an electrode. The carboxyl group-containing organic resins B1 to B4 synthesized in Reference Example were respectively dissolved in an aromatic petroleum fraction having a boiling point range from 130 to 180°C according to the compositions shown in Table 2. Also, a resol type phenol resin B5 that was an organic resin for comparison was dissolved in ethylene glycol diethyl ether. The carbon particles shown in Table 2 were respectively added in the ether solution, which was then mixed by a three-roll until the carbon particles were uniformly dispersed to prepare a conductive paste. This conductive paste was allowed to stand at ambient temperature for 24 hours to observe the degree of separation of the

carbon particles. The results as shown in Table 2 were obtained.

[0030]

This conductive paste was screen-printed on a stainless current collector such that the thickness of the coating film after dried was 2 to 4 μm and then the above electrode was stuck to the conductive paste under pressure, followed by drying under heating at 130°C for 15 minutes to bond the electrode with the current collector. In Example 4, however, the drying operation was carried out under heating at 120°C for 30 minutes and then the bonding operation was carried out on a 150°C hot plate. Also, in Comparative Example 2, the coating layer was cured by heating at 200°C for 30 minutes. The adhesive layers obtained in this manner were subjected to a test to measure the volume resistance of each adhesive layer.

[0031]

Two electrode elements comprising the carbon electrode and current collector which were bonded with each other in this manner were stuck to each other under pressure through a separator made of a polypropylene porous film such that these elements were facing each other. The elements were filled with an electrolytic solution prepared by dissolving 1 mol of tetraethylammonium perchlorate in 1,000 ml of mixture solution of propylene carbonate and dimethoxyethane (mol ratio: 1 : 1) to make an electric double-layer condenser. As to the capacity of the capacitor obtained in this manner, the initial value of the capacity and the value of the capacity after 50 heat cycles (−20°C, 30 minutes to 90°C, 30 minutes in one cycle) were measured by the method described in the publication of JP-A 2-2186808. Also, the condition of the electrode after the heat cycle test was

finished was observed.

[0032]

These results are shown in Table 2 in a manner as to compare Examples 1 to 4 using the conductive adhesive of the present invention with Comparative Example 1 using carbon particles having a lower pH value and Comparative Example 2 using a resol type phenol resin as an organic resin.

[0033]

[Table 2]

Table 2

			Examples					Comparative Examples	
			1	2	3	4	5	1	2
Composition	Organic resin	Kind	B1	B1	B3	B2	B4	B1	B5
		Amount (parts)	60	70	70	70	55	70	70
	Carbon particles	Size (angstroms)	400	400	400	760	760	180	400
		pH	6.8	6.8	6.8	7.5	7.5	3.2	6.8
		Amount (parts)	40	30	30	30	45	30	30
Nonvolatile content (wt%)		41	39	42	42	34	37	43	
Stability of the conductive paste*1			○	○	○	○	○	×	○
Coating film thickness (μm)			3	4	4	4	4	4	3
Volume resistivity (Ω-cm)			1.0	1.5	1.7	1.2	1.3	0.7	0.2
Capacity (F) Initial value			1.5	1.4	1.5	1.5	1.3	1.5	1.5
After heat cycles			1.5	1.4	1.5	1.5	1.3	1.4	0.3
Condition of electrode*2			○	○	○	○	○	○	×

(Note) *1 ○: Non-separated; ×: Separated

*2 After heat cycles, ○: Normal; ×: Peeled

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